

Attachment 6

CPG Partitioning Approach in Draft RI Appendix O versus Appendix G

The CPG model described in the Draft RI represents partitioning of hydrophobic contaminants to only detrital particulate organic carbon (POC). The partitioning approach described in Appendix O of the Draft RI is inconsistent with the analysis presented in Appendix G, which provides a better estimate of the distribution of contaminants between the dissolved and particulate phases based on the high volume chemical water column monitoring (HV-CWCM) data.

This memo summarizes checks of the CPG's analysis of the HV-CWCM data and an evaluation of the effect of using CARP-derived partition coefficients versus HV-CWCM-derived partition coefficients.

To verify the calculation methods and results of the CPG's evaluation of contaminant partitioning using the HV-CWCM data, an attempt was made to reproduce the values presented in the CPG's RI Appendix G tables. Based on the checks of the CPG's analysis of the HV-CWCM data, the following methods and assumptions were necessary to reproduce the CPG's values: 1) all non-detect concentrations were set at half of the detection limit; 2) post-PUF filtrate concentrations were not added to the total dissolved concentrations; 3) field duplicate sample concentrations were averaged prior to the partition coefficient calculations; 4) When excluding non-detected dissolved concentrations in Appendix G, Tables 3b, 4b, and 5b, the CPG excluded dissolved concentrations if at least one of the two PUF concentrations was a non-detect. The calculated total particulate concentration, total dissolved concentration and partition coefficient values (Log KD, 2-Phase Log KOC and 3-Phase Log KOC) were reproduced with some small differences in the second decimal place due to round-off.

Using the computed particulate and dissolved chemical concentrations, which were matched to the Appendix G values, the percent dissolved measurements for 2,3,7,8-TCDD presented in the CPG's RI Appendix O Figure 3-9a were successfully reproduced. The values are plotted as blue bars in Figure 1 below.

Based upon the CPG's description in Appendix O of the Draft RI, the multi-phase partitioning sorption Models 1 and 2 represent full equilibrium and partial equilibrium, respectively. The full equilibrium model assumes that chemical mass is instantaneously distributed across all phases. The partial equilibrium model, which was chosen as the basis for partitioning in the water column within CPG RCATOX application, assumes that water column chemical mass is instantaneously distributed between the detrital carbon and freely dissolved phases while sorption to algae and DOC are not considered. Both model calculations included temperature and salinity corrections. Since the station at RM4.2 did not have a salinity measurement for Event 1, the salinity recorded during Event 2 was used. Model simulated temperature values were used for temperature corrections because the temperature data were not available. Note: temperature data were collected over the course of each sample collection, and are provided in the HV-CWCM reports in PDF tables, but those values were not available in EQuIS or on SharePoint in a user friendly format. The model calculated percent dissolved values for the Newark Bay and Kill van Kull stations differed slightly from what was presented in Appendix O Figure 3-9a. This was likely due to uncertainties associated with the temperatures used.

The sorption model calculations using the CARP organic carbon partition coefficient (KOC) value for 2,3,7,8-TCDD, shown on Figure 1 reproduce the results presented in Appendix O Figure 3-9a. The effect of replacing the CARP-derived KOC with the KOC value derived from the HV-CWCM data (Appendix G,

Table 5a) is shown on Figure 2. Using the Appendix G, 3-phase partition coefficient value for 2,3,7,8-TCDD (Figure 2), Model 1 captures the fraction dissolved measurements better at most stations. Using the Appendix G partition coefficient the root mean square deviation (RMSD) between the measured and predicted fraction dissolved is reduced from 29% to 9.1%. Using the Appendix G 3-phase partition coefficient to represent two phase partitioning results in an underestimate of the dissolved chemical fractions, increasing the RMSD from 9.5% to 12%. Overall using the 3-phase partition coefficient based on the RI data (Appendix G) to represent 3-phase partitioning (Model 1) does the best job of reproducing the fraction dissolved, with the additional benefit of appropriately representing the impact of DOC on the bioavailable fraction of the dissolved chemical.

A similar analysis was performed for Tetra-PCB, however, the HV-CWCM-derived Log KOC value (6.36) is not very different from the CARP value (6.27), so the results based on the CARP value (Figure 3) are similar to the results calculated with the HV-CWCM-derived value (Figure 4). Model 1 yields approximately the same RMSD values of 18% using both the CARP and Appendix G Log KOC values. Similarly, for Model 2 the RMSD is approximately 21% using both the CARP and Appendix G Log KOC values. These results suggest that Model 1 does a better job than Model 2 reproducing the fraction dissolved for Tetra-PCB, but the CARP and HV-CWCM based 3-phase partition coefficients yield similar results because of the similar Log KOC values.

As a final comparison between the approaches discussed above Figure 5 presents the RMSD for the computed fraction dissolved for 2,3,7,8-TCDD and Tetra-PCB. In addition to using the CPG's Model 1 and 2 with the CARP and Appendix G 3-phase partition coefficients, the computed deviations are also presented using the assumption of 2-phase partitioning using the 2-phase partition coefficient derived in Appendix G. Note that using the standard 3-phase partitioning approach (CPG Model 1) with the Appendix G 3-phase partition coefficients does the best job of reproducing the HV-CWCM measured fraction dissolved. In the case of Tetra-PCB the difference between the two 3-phase partitioning approaches is small due to the small difference in the CARP and Appendix G values for the Tetra-PCB 3-phase partition coefficients. The 3-phase partitioning approach has the added benefit of representing the impact of DOC on contaminant bioavailability.

The CPG's analysis of partitioning in the LPR, including comparison of calculated contaminant dissolved and particulate fractions to the HV-CWCM data, is presented in RI Appendix G. The CPG also used the HV-CWCM data to test partition coefficients determined from CARP data (RI Appendix O) and concluded that contaminant dissolved fractions were under-predicted with the CARP-derived partition coefficients. Rather than use the partition coefficients derived from the HV-CWCM data (Appendix G), the contaminant fate and transport modeling in the RI is based on using the CARP 3-phase partitioning coefficients with partitioning to DOC and algae eliminated. The elimination of these two partitioning phases is described as necessary to reproduce the dissolved fractions observed in the HV-CWCM data. A more reasonable approach is to retain partitioning among detrital POC, algal POC, DOC, and freely dissolved phases, with partition coefficients derived from the HV-CWCM RI data. The CPG must revise their modeling approach to include partitioning among the detrital POC, algal POC, DOC, and freely dissolved phases consistent with the three phase partitioning analysis based on the HV-CWCM RI data (Appendix G).

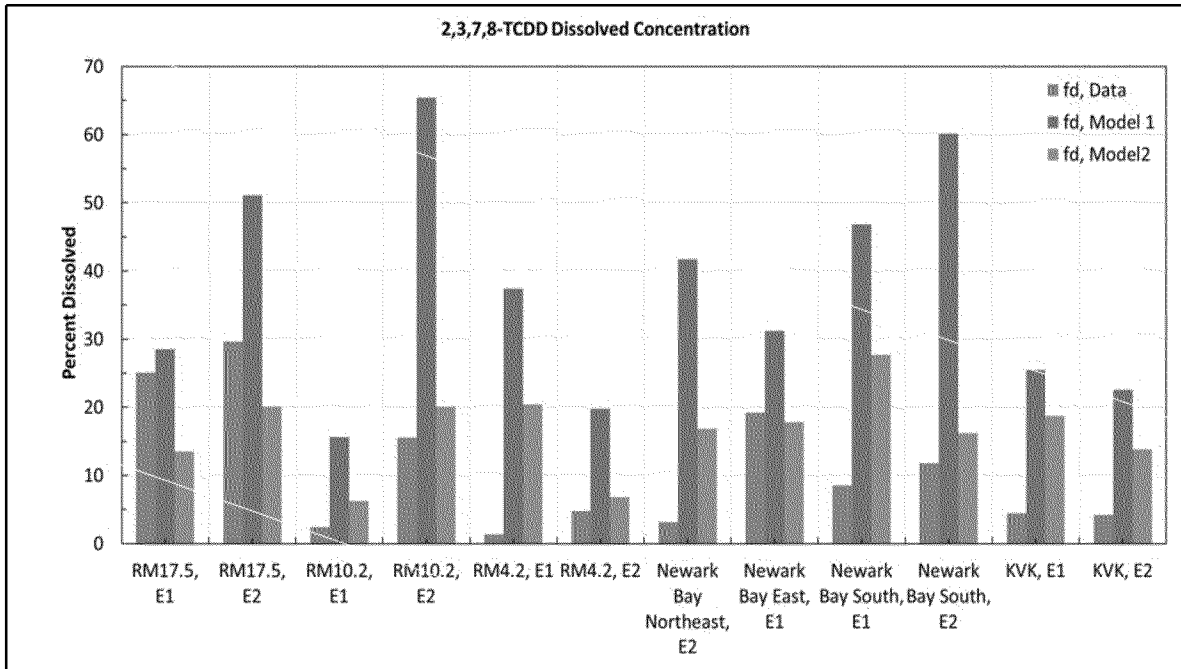


Figure 1. Comparison of HV CWCM 2,3,7,8-TCDD Dissolved Fraction Measurements to Two Sorption Models (CARP Log K_{oc} = 6.81)

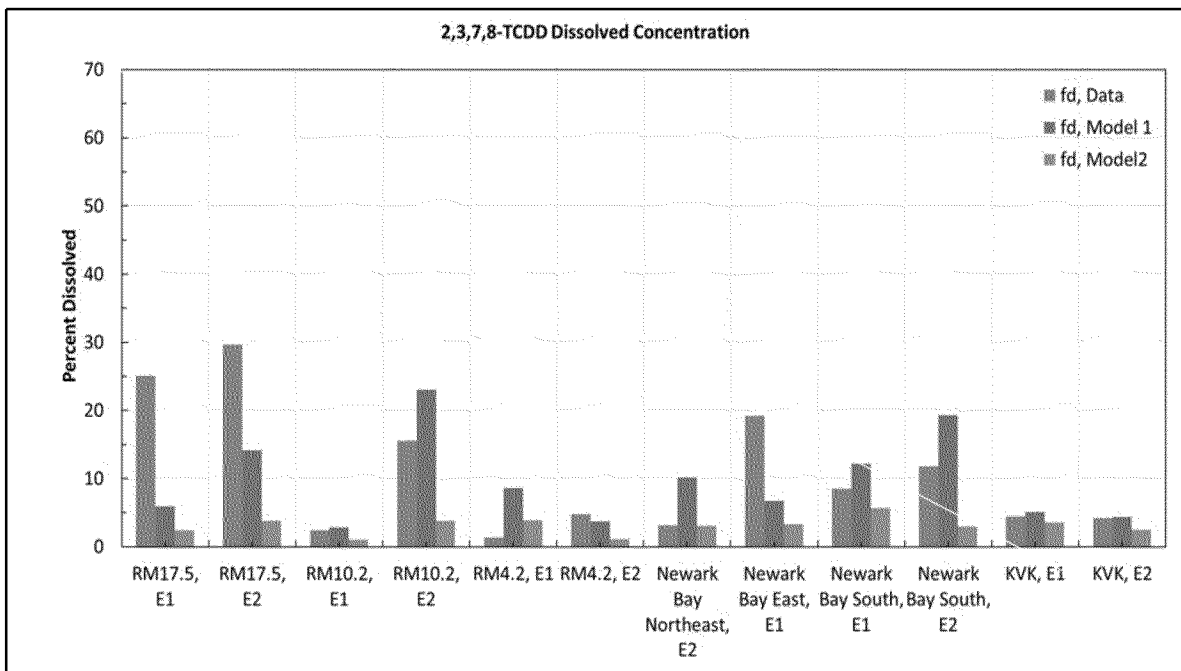


Figure 2. Comparison of HV CWCM 2,3,7,8-TCDD Dissolved Fraction Measurements to Two Sorption Models (Appendix G Log K_{oc} = 7.61)

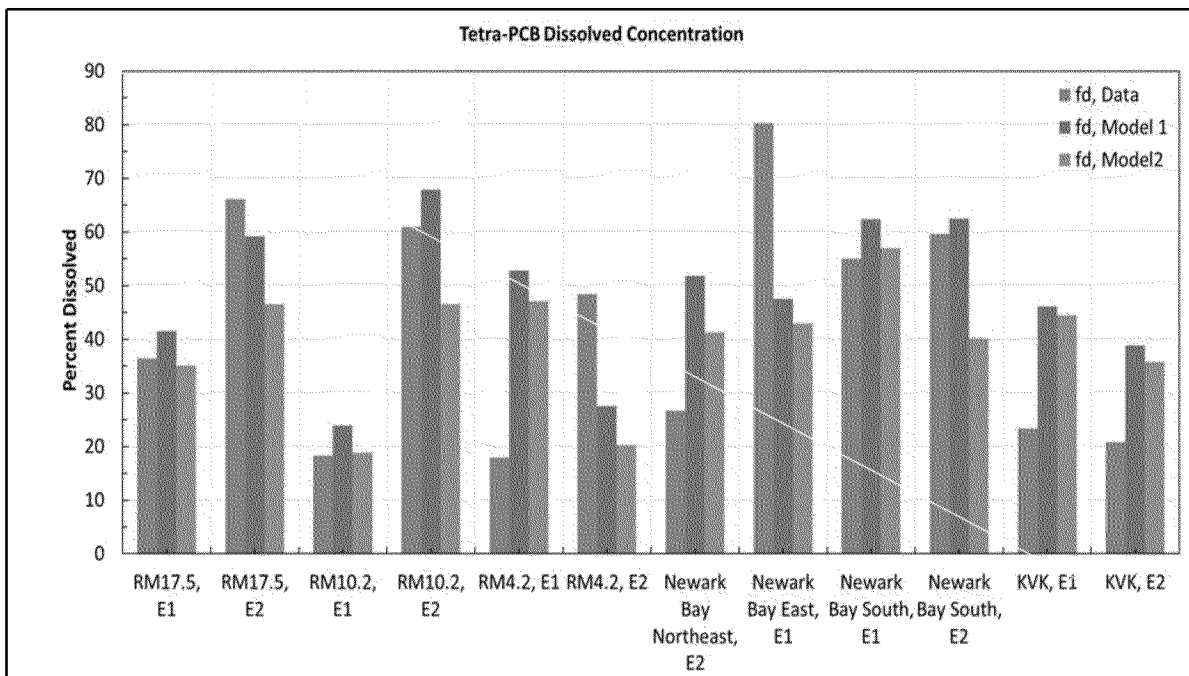


Figure 3. Comparison of HV CWCM Tetra-PCB Dissolved Fraction Measurements to Two Sorption Models (CARP Log K_{oc} = 6.27)

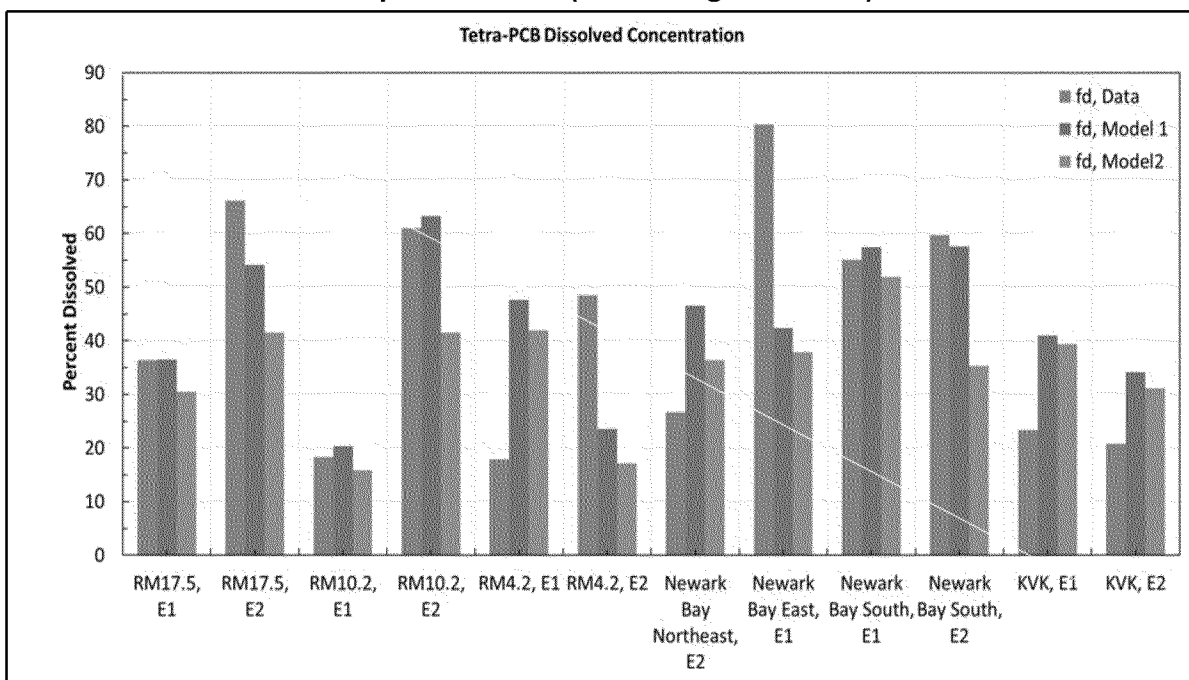


Figure 4. Comparison of HV CWCM Tetra-PCB Dissolved Fraction Measurements to Two Sorption Models (updated Log K_{oc} = 6.36)

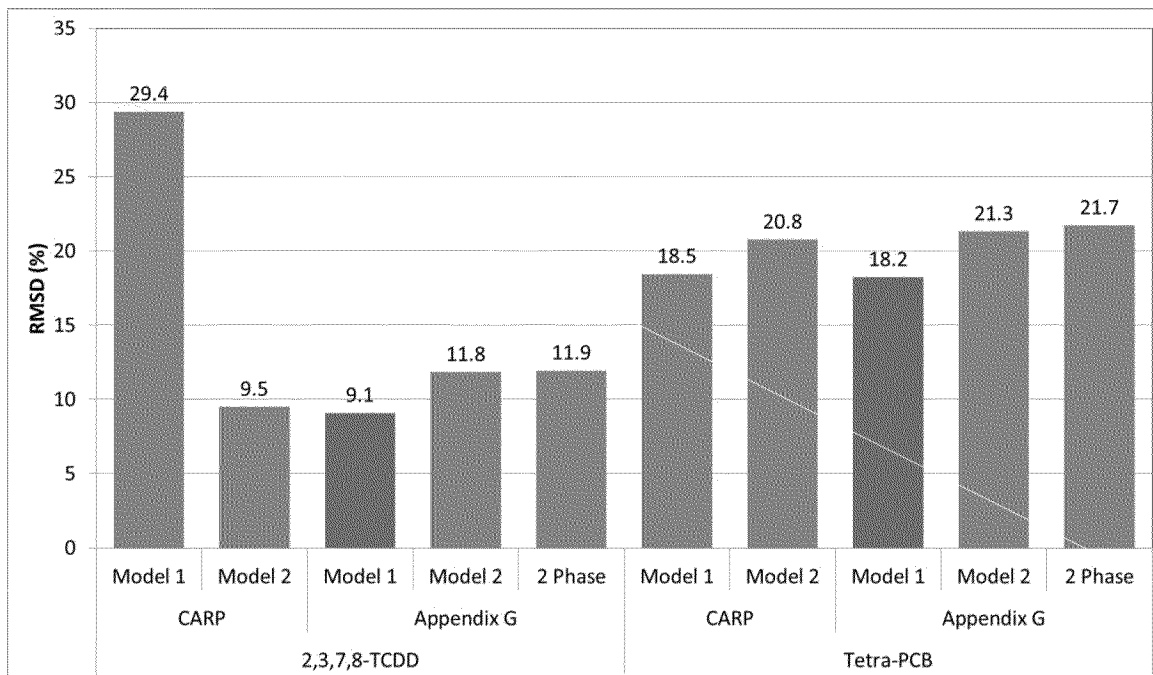


Figure 5. Root Mean Square Deviation of Partitioning Model Predicted Percent Dissolved Compared to the HV-CWCM Data